NAREL Standard Operating Procedure for Isotopic Determination of Americium, Plutonium, Thorium, and Uranium in Solid Matrices Following Sodium Hydroxide Fusion

AM/SOP-41

Revision 3

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AM/SOP-41

Revision History

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0	AM/SOP-41	Shane Knockemus	2016-06-17
1	AM/SOP-41	Shane Knockemus	2017-09-19
2	AM/SOP-41	Shane Knockemus	2018-06-01
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Changes Between Revisions 2 and 3	
Section	**Description of Changes**
8.8.6	Changed from: "Hydrochloric acid (4 M) + hydrofluoric acid (0.2 M) + 0.002 M $TiCl_3$. Add 0.1 mL of 20 % $TiCl_3$ solution per 100 mL needed. Prepare fresh daily as needed." To read: "Hydrochloric acid (4 M) + hydrofluoric acid (0.2 M) + 0.002 M $TiCl_3$. Add 0.2 mL of 20 % $TiCl_3$ solution per 100 mL needed. Prepare fresh daily as needed."
12.2.8	Added step.

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1.0 PURPOSE

1.1 This standard operating procedure (SOP) describes a method for radiochemical analysis of americium, plutonium, thorium, and uranium using extraction chromatography for the chemical separation of the analytes from a variety of solid matrices following total dissolution by means of sodium hydroxide fusion.

2.0 SCOPE AND APPLICATION

2.1 This method is applicable for the measurement of ^{241}Am, ^{238}Pu, ^{239}Pu, ^{227}Th, ^{228}Th, ^{230}Th, ^{232}Th, ^{234}U, ^{235}U, and ^{238}U in a variety of solid environmental matrices.

NOTE: NAREL has not yet approved this method for the measurement of ^{241}Am.

2.2 The detection and quantification capabilities of this method are functions of sample size, interferences, instrument backgrounds, counting efficiency, and count time. The actual minimum detectable concentration (MDC) for each sample may be different based on any of these variables. For soil samples, using a 1 g aliquot and a 1000 min count time, the expected MDC is 0.08 pCi/g for ^{238}Pu and ^{239}Pu, 0.14 pCi/g for ^{230}Th, 0.12 pCi/g for ^{235}U, and 0.10 for ^{232}Th, ^{234}U, and ^{238}U.

3.0 DEFINITIONS

3.1 **R value** – the ratio of observed activity divided by the actual amount of added activity, a measure of recovery.

NOTE: See *NAREL Common Terminology* (DR/T-1) for the definitions of other terms and acronyms used in this document.

4.0 SUMMARY OF METHOD

4.1 This procedure describes a method for the isotopic determination of americium, plutonium, thorium, and uranium from solid matrices following total dissolution by means of sodium hydroxide fusion. It involves the use of a tandem arrangement of the TEVA™ and TRU or DGA resin cartridges (available from Eichrom Technologies). The resin cartridges used effectively separate and isolate Am, Pu, Th, and U from environmental matrices. The cartridges are stacked so that the effluent from the TEVA resin cartridge flows into the TRU or DGA resin cartridge. The oxidation states of the elements of interest in the load solution are as follows: Am^{+3}, Pu^{+4}, Th^{+4}, and U^{+6}. Any Th or Pu present in the sample will be retained on the TEVA resin. Any uranium in the sample will pass through the TEVA resin cartridge and be sorbed onto the TRU resin cartridge. Any americium in the sample will pass through the TEVA resin cartridge and be sorbed onto the DGA resin cartridge.

4.2 The tandem cartridge arrangement will then be separated and the elements of interest will be selectively eluted. The elements of interest will then be coprecipitated as a fluoride, and radioassayed by alpha-particle spectrometry.

4.3 If there is an analyte that is not requested for analysis there are steps within the procedure that can be altered to accommodate this without affecting the result of the other analyses. For example, if Th analysis is not requested, the use of the TEVA cartridge is still necessary, but the elution, purification, and co-precipitation of Th is no longer necessary. Other scenarios do exist.

5.0 INTERFERENCES

5.1 Actinides with unresolvable alpha energies such as ^{241}Am and ^{238}Pu, ^{237}Np and ^{234}U, ^{232}U and ^{228}Th, ^{228}Th and ^{241}Am, ^{232}U and ^{243}Am, and ^{228}Th and ^{238}Pu must be chemically separated to enable a reliable measurement. This method separates all of these isotopes effectively.

5.2 The presence of Fe^{+3} can interfere with the retention of the actinides on the resin. Any Fe^{+3} that is present in the sample must be reduced to Fe^{+2} with the addition of ascorbic acid so that it will not interfere with desired chemical reactions.

5.3 The presence of certain matrix constituents commonly associated with environmental samples, such as phosphates, sulfates, and oxalates, can cause interferences. The addition of Al^{+3} effectively complexes such ions so that they do not interfere with the analysis. In fact, the presence of Al^{+3} actually increases the retention factor of Am to the TRU cartridge. There may be instances when increasing the Al^{+3} concentration in the nitric acid + aluminum nitrate load solution can be beneficial to radiochemical separation and recovery. If a higher concentration of Al^{+3} is needed, increase the amount of aluminum nitrate added in the dissolution of the sample aliquot.

5.4 Americium and uranium analysis should not be run sequentially. If Am and U are requested for the same sample, they should be analyzed from separate aliquots.

6.0 ROLES AND RESPONSIBILITIES

6.1 Unless otherwise noted, the radiochemist is responsible for performing all steps of this procedure. These responsibilities include grouping samples into QC batches, performing chemical separations and recording all data in laboratory notebooks.

6.2 Personnel in the Nuclear Counting Laboratory calibrate and maintain alpha-particle spectrometers, use them to analyze prepared samples, and perform the first review of analytical results.

6.3 The NAREL Radiochemistry Data Coordinator (RDC) performs a second review of each analysis performed using this method.

6.4 The NAREL QA Chemist is responsible for preparing ^{230}Th, ^{239}Pu, and ^{238}U spiking solutions, and appropriate tracer solutions.

7.0 EQUIPMENT AND SUPPLIES

7.1 Assorted glassware.

7.2 Stainless steel planchets, 32 mm diameter.

7.3 Petri dishes.

7.4 Tweezers.

7.5 Alpha spectrometric system consisting of multichannel analyzer, biasing electronics, printer, silicon surface barrier detectors, vacuum pump, and chamber.

7.6 Calibrated analytical balance, readability 0.1 mg or less.

7.7 Calibrated top-loading balance.

7.8 Calibrated Eppendorf® auto pipets, assorted volumes.

7.9 Vacuum box (available from Eichrom Technologies).

7.10 Yellow tips (available from Eichrom Technologies).

7.11 Inner support tips (available from Eichrom Technologies).

7.12 25 mm Resolve Filter (0.1 µm pore size) in disposable funnel, or equivalent filter apparatus.

7.13 Cartridge reservoir with various volumes as needed.

7.14 50 mL disposable centrifuge tubes.

8.0 REAGENTS AND STANDARDS

8.1 Reagent grade chemicals (or better) shall be used in all tests.

8.2 Reagent water in this method is laboratory de-ionized water which is treated by a point of use filtration system to ≥18.0 MΩ·cm resistivity (see the De-ionized Water System section in the Equipment chapter of the *NAREL Radiochemistry Quality Assurance Manual*) which is equivalent to ASTM Type 1, and shall be interference free. Analysis of a method blank must verify that the water is free from interferences.

8.3 Ammonium bioxalate solution, (0.1 M). Dissolve 6.3 g oxalic acid and 7.1 g ammonium oxalate in 900 mL of water, and dilute to 1 L.

8.4 Ammonium oxalate, $(NH_4)_2C_2O_4 \cdot H_2O$, [CAS# 6009-70-7].

8.5 Ascorbic acid, powder, $C_6H_8O_6$, [CAS# 50-81-7].

8.5.1 Ascorbic acid solution (1.5 M). Dissolve 26.4 g of ascorbic acid powder in 75 mL deionized water and dilute to 100 mL. Slight warming might be helpful to dissolve ascorbic acid powder completely. Make fresh solution monthly.

8.6 Cerium (III) nitrate hexahydrate, $Ce(NO_3)_3 \cdot 6H_2O$, [CAS# 10294-41-4].

8.6.1 Ce^{+3} carrier (500 mg/mL): Dissolve 0.155 g cerium (III) nitrate hexahydrate in 50 mL of deionized water and dilute to 100 mL (0.5 mg/mL Ce^{+3}).

8.7 Ethyl alcohol solution or equivalent, [CAS# 141-78-6].

8.8 Hydrochloric acid, HCl, (concentrated, 12 M), [CAS# 7647-01-0].

8.8.1 Hydrochloric acid (6 M): Add 500 mL of concentrated HCl to 400 mL of deionized water and dilute to 1 L with deionized water.

8.8.2 Hydrochloric acid (4 M): Add 333 mL of concentrated HCl to 500 mL of deionized water and dilute to 1 L with deionized water.

8.8.3 Hydrochloric acid (3 M): Add 250 mL of 12 M HCl to 500 mL of deionized water and dilute to 1 L with deionized water.

8.8.4 Hydrochloric acid (0.25 M): Add 20.8 mL of 12 M HCl to 800 mL of deionized water and dilute to 1 L with deionized water.

8.8.5 Hydrochloric acid (4 M) + hydrofluoric acid (0.2 M) solution. Add 7.14 mL of 29 M HF to 1000 mL of 4 M HCl.

8.8.6 Hydrochloric acid (4 M) + hydrofluoric acid (0.2 M) + 0.002 M $TiCl_3$. Add 0.2 mL of 20 % $TiCl_3$ solution per 100 mL needed. Prepare fresh daily as needed.

8.8.7 Hydrochloric acid (0.1 M) + hydrofluoric acid (0.05 M) solution: Add 1.8 mL 29 M HF and 8.3 mL 12 M HCl to 500 mL of water. Dilute to 1 L.

8.8.8 Hydrochloric acid (0.1 M) – hydrofluoric acid (0.05 M) – $TiCl_3$ (0.01 M). Add 2 mL of 20 % $TiCl_3$ solution per 100 mL of 0.1 M HCl + 0.05 M HF solution. Prepare fresh daily as needed. Vary amounts of $TiCl_3$ appropriately based on strength of $TiCl_3$ solution.

8.9 Hydrofluoric acid, HF, (concentrated, 29 M), [CAS# 7664-39-3].

8.10 Hydrogen peroxide, 30 %, [CAS# 7722-84-1].

8.11 Iron (III) nitrate nonahydrate, $Fe(NO_3)_3 \cdot 9H_2O$.

8.11.1 Fe^{+3} (5 mg/mL). Dissolve 18.1 g iron (III) nitrate nonahydrate in 300 mL of deionized water. Dilute to 500 mL with deionized water.

8.12 Nitric acid, HNO_3, (concentrated, 16 M), [CAS# 7697-37-2].

8.12.1 Nitric acid (8 M): Add 500 mL of 16 M HNO_3 to 400 mL of deionized water and dilute to 1 L with deionized water.

8.12.2 Nitric acid (6 M): Add 375 mL of 16 M HNO_3 to 500 mL of deionized water and dilute to 1 L with deionized water.

8.12.3 Nitric acid (3 M): Add 187.5 mL of 16 M HNO_3 to 500 mL of deionized water and dilute to 1 L with deionized water.

8.12.4 Nitric acid (0.1 M): Add 6.25 mL of 16 M HNO_3 to 800 mL of deionized water and dilute to 1 L with deionized water.

8.12.5 Nitric acid (0.05 M): Add 3.13 mL of 16 M HNO_3 to 800 mL of deionized water and dilute to 1 L with deionized water.

8.12.6 Nitric acid (3 M) / hydrofluoric acid (0.25 M) solution: Add 187.5 mL 16 M HNO_3 and 8.6 mL 29 M HF to 700 mL of deionized water and dilute to 1 L with deionized water.

8.13 Oxalic acid dihydrate, $H_2C_2O_4 \cdot 2H_2O$, (0.1 M) [CAS# 6153-56-6].

8.14 Sodium nitrite, $NaNO_2$, [CAS#: 7632-00-0].

8.14.1 Sodium nitrite solution (3.5 M). Dissolve 6.1 g $NaNO_2$ in 25 mL of deionized water. Prepare fresh daily as needed.

8.15 Titanium (III) chloride, $TiCl_3$, (10–20 % in hydrochloric acid) [CAS# 7705-07-9]. Replace within six months after opening. Store in amber bottle away from direct sunlight.

8.16 TRU Resin pre-packed 2 mL resin cartridge (available from Eichrom Technologies).

8.17 TEVA Resin pre-packed 2 mL resin cartridge (available from Eichrom Technologies).

8.18 DGA Normal Resin pre-packed 2 mL resin cartridge (available from Eichrom Technologies).

9.0 SAFETY

9.1 All procedures performed at NAREL must be conducted following the requirements detailed in the *NAREL Chemical Hygiene Plan* (HS/M-2) and the *NAREL Radiation Safety Manual* (HS/M-1). Safety precautions associated with handling of chemical reagents, solutions, and all samples are the primary responsibility of the analyst. Any spills or accidents involving hazardous, corrosive, or toxic material must be immediately resolved.

9.2 All NAREL laboratory personnel are expected to use good laboratory practices. Most of the safety training is provided by the SHEM officer. The analyst is expected to comply with all directives given by the SHEM officer, and must take necessary precautions to prevent exposure or injury to both self and co-workers.

9.3 Unnecessary or prolonged exposure to laboratory chemicals should be avoided.

9.4 Aluminum nitrate nonahydrate, $Al(NO_3)_3 \cdot 9H_2O$, [CAS# 7784-27-2], is a strong oxidizer; contact with other material may cause fire. Harmful if swallowed or inhaled. Causes irritation to skin, eyes and respiratory tract. Inhalation may result in coughing and shortness of breath. Ingestion may cause gastroenteritis and abdominal pain. Avoid contact with skin and eyes by using appropriate protective clothing and equipment. Use only with adequate ventilation. Keep separate from combustible, organic, or any other readily oxidizable materials. Store in a tightly closed container.

9.5 Ammonium oxalate, $[(NH_4)_2C_2O_4 \cdot H_2O]$, [CAS# 6009-70-7], is poisonous and may be fatal if inhaled or ingested. Contact with skin or eyes can cause severe irritation and pain and may cause burns. Ammonium oxalate must be kept in a tightly closed container and stored in a dry, ventilated area, away from incompatible substances such as strong acids. Wash hands thoroughly after use.

9.6 Ascorbic acid, powder, $C_6H_8O_6$, [CAS# 50-81-7], is relatively non-hazardous but may cause mild irritation to the respiratory tract if inhaled, and mild irritation to skin and eyes upon contact. Avoid contact with skin and eyes by using appropriate protective clothing and equipment. Use with adequate ventilation. Store in a tightly closed container; keep away from heat.

9.7 Cerium (III) nitrate hexahydrate, $Ce(NO_3)_3 \cdot 6H_2O$, [CAS# 10294-41-4], is a strong oxidizer; contact with other material may cause fire. Causes eye and skin irritation; may be harmful if absorbed through the skin. May cause respiratory tract irritation; may be harmful if inhaled. May cause irritation of the digestive tract. Avoid contact with skin and eyes by using appropriate protective clothing and equipment. Use only with adequate ventilation. Keep separate from incompatibles, combustibles, or other readily oxidizable materials. Hygroscopic. Store in a tightly closed container.

9.8 Ethyl alcohol (ethanol), C_2H_5OH, [CAS# 64-17-5], is flammable as a liquid and as a vapor. Inhalation may cause drowsiness and irritation to the respiratory tract. Avoid skin and eye contact by using appropriate protective clothing. Use only in a well-ventilated area away from open flames and ignition sources. Store in containers approved for ethyl alcohol.

9.9 Hydrochloric acid, HCl, [CAS# 7647-01-0], is harmful if swallowed, inhaled, or ingested. It can cause serious damage to eyes and skin. Ingestion can cause burns around the mouth, throat, and esophagus with irritation and pain. Hydrochloric acid causes chemical burns following contact with skin and eyes. Inhalation can cause toxic effects and may be fatal. Use hydrochloric acid only with adequate ventilation and appropriate protective clothing. Always release caps slowly to ensure slow dissipation of vapors. Store concentrated hydrochloric acid in the original container, securely sealed, in a cool, dry, well-ventilated area, away from alkaline materials, galvanized steel, and zinc. Avoid strong bases. Do not discharge into sewer or waterways.

9.10 Hydrofluoric acid, HF, [CAS# 7664-39-3], is a highly reactive chemical. It must be stored in plastic containers, and away from light, heat, and strong bases. Hydrofluoric acid is highly destructive to tissue and may be fatal if inhaled, swallowed, or absorbed through the skin. Hydrofluoric acid should be used only by persons trained and familiar with appropriate safety precautions.

9.11 Hydrogen peroxide, 30 %, [CAS# 7722-84-1]. Harmful if swallowed. Causes severe eye burns. Wear personal protective equipment. Ensure adequate ventilation.
Do not get in eyes or on skin or on clothing. Wash immediately with water for at least 15 minutes.

9.12 Iron (III) nitrate nonahydrate, $Fe(NO_3)_3 \cdot 9H_2O$, [CAS# 7782-61-8]. May intensify fire. Oxidizer. Causes skin irritation. Causes serious eye irritation. May cause respiratory irritation. Store away from clothing or combustible material.

9.13 Nitric acid, HNO_3, [CAS# 7697-37-2], is poisonous, reactive, and a strong oxidizer. Contact with other materials may cause fire. It can cause burns to body tissues and may be fatal if ingested or inhaled. Vapors are irritating to eyes and mucous membranes. Use only with adequate ventilation and proper protective clothing and gloves. Nitric acid is incompatible with most substances, especially strong bases, metallic powders, carbides, and combustible organics. Store away from light and heat.

9.14 Oxalic acid dihydrate, $H_2C_2O_4 \cdot 2H_2O$, [CAS# 6153-56-6], is a poison and corrosive; may be fatal if swallowed or inhaled. Causes severe irritation and burns to skin, eyes, and respiratory tract. Harmful if inhaled or absorbed through skin. May cause kidney damage. Harmful if inhaled: can cause severe irritation and burns of nose, throat and respiratory tract. Toxic: ingestion may cause burns, nausea, severe gastroenteritis and vomiting, shock and convulsions. May cause renal damage; estimated fatal dose is 5–15 g. Contact with skin can cause severe irritation and burns; may be absorbed through skin. Contact with eyes can cause severe irritation and may produce corrosive effects. Avoid contact with skin and eyes by using appropriate protective clothing and equipment. Use only with adequate ventilation. Store in a tightly closed container; keep away from heat and incompatibilities.

9.15 Sodium nitrite, $NaNO_2$, [CAS#: 7632-00-0], is a strong oxidizer; contact with other material may cause fire. Heat, shock, or contact with other material may cause fire or explosive decomposition. Harmful if swallowed, inhaled or absorbed through skin. Causes irritation to skin, eyes and respiratory tract. Toxic: inhalation causes irritation to the respiratory tract and systemic poisoning with symptoms paralleling indigestion. Ingestion can irritate the mouth, esophagus, stomach, etc.; excessive amounts affect the blood and blood vessels (estimated lethal dose 1–2 g). Contact with skin and eyes causes irritation, redness, and pain; may be absorbed through skin, causing systemic poisoning. Avoid contact with skin and eyes by using appropriate protective clothing and equipment. Use only with adequate ventilation. Keep separate from incompatibles, combustibles, organic or any other readily oxidizable materials. Store in a tightly closed container away from heat.

9.16 Titanium chloride, $TiCl_3$, [CAS# 7705-07-9], is a flammable solid and can cause severe eye and skin burns. Replace within six months after opening. Store in amber bottle away from direct sunlight.

9.17 Safety data sheets (SDSs) are available to all personnel involved in chemical analysis. It is the responsibility of each analyst to be familiar with chemicals used during an analysis.

9.18 Refer to the *NAREL Chemical Hygiene Plan* (HS/M-2) for verification of appropriate safety and health practices.

10.0 SAMPLE COLLECTION, PRESERVATION, AND STORAGE

10.1 Soil samples can be shipped to the laboratory in either plastic or glass containers. No preservation is required.

10.2 Special handling such as refrigeration or freezing may be required for samples of other matrices such as animal tissue or vegetation.

10.3 Samples for actinides analysis do not require refrigeration during storage.

11.0 CALIBRATION AND STANDARDIZATION

11.1 A detailed procedure for preparing the ^{232}U tracer is presented in *NAREL Standard Operating Procedure for Preparation of Self-Cleaning U-232 Tracer Solution* (AMS/SOP-6).

11.2 All fixed volume pipets used must be calibrated and checked in accordance with the *NAREL Standard Operating Procedure for Calibration, Use, and Maintenance of Pipets* (SE/SOP-4).

11.3 All balances used must be calibrated and checked in accordance with the *NAREL Standard Operating Procedure for Calibration of Balances* (SE/SOP-1).

11.4 All alpha spectrometers must be calibrated in accordance with the *NAREL Standard Operating Procedure for Calibration and Use of Alpha Spectrometers Using AlphaVision* (NC/SOP-8).

12.0 PROCEDURE

12.1 *Cartridge Preparation*

12.1.1 For each sample to be analyzed for Pu, Th, or U place one TEVA resin cartridge and one TRU resin cartridge in a tandem arrangement so that the effluent from the TEVA cartridge flows into the TRU cartridge. For each sample to be analyzed for Pu, Th, or Am place one TEVA resin cartridge and one DGA resin cartridge in a tandem arrangement so that the effluent from the TEVA cartridge flows into the DGA cartridge. Fit each cartridge arrangement with an appropriately sized sample reservoir.

12.1.2 All steps in the procedure may make use of a vacuum box to speed up flow through the cartridges. Generally, the flow rate is set at 1–2 mL/min.

12.1.3 Condition the cartridges with 5 mL of 3 M HNO_3. Allow them to drain. Discard the effluent.

12.2 *Chemical Separation*

12.2.1 Obtain the dissolved sample. If particles are observed in the solution, centrifuge the sample, collect the supernate and discard the solids. Visible solids will clog the frit on reservoir which will inhibit the flow rate of the sample.

12.2.2 Add 0.2 mL of 5 mg/mL Fe^{+3} solution.

12.2.3 Add 1 mL of 1.5 M ascorbic acid. Samples high in Fe^{+3} might require additional ascorbic acid. Swirl the sample to mix. Wait ~2 min.

12.2.4 Add 1 mL of 3.5 M $NaNO_2$. Thoroughly mix the sample. Wait ~10 min.

12.2.5 Transfer each load solution from into the appropriate reservoir.

12.2.6 Allow the solution to pass through the stacked TEVA + TRU or TEVA + DGA cartridges with the vacuum adjusted to flow rate of ~ 1 mL/min.

12.2.7 Add 5 mL of 3 M HNO_3 containing 50 µL of 30 % H2O2 to the reservoir on the top cartridge and allow it to drain. Discard the effluent.

12.2.8 Add 15 mL of 3 M HNO_3 to each reservoir. Allow this rinse to drain through both cartridges at a flow rate of ~2 mL/min. Discard the effluent.

12.2.9 Turn off the vacuum. Separate the TEVA + TRU or TEVA + DGA tandem arrangement. If analyzing for Th or Pu proceed to step 12.3. Place new reservoir on TEVA cartridge. If analyzing for U on TRU, proceed to step 12.4. If analyzing for Am on DGA, proceed to step 12.5.

12.3 *Purification and Elution of Thorium and Plutonium*

12.3.1 Place new reservoir on TEVA cartridge.

12.3.2 Rinse the TEVA cartridge with 10 mL of 3 M HNO_3. Discard the effluent. Record the date and time of this final rinse as the "Thorium Separation Time."

12.3.3 Place a clean 50 mL polypropylene centrifuge tube labeled with sample number and "Th" below the appropriate cartridge. Place new yellow tips on TEVA cartridges.

12.3.4 Add 15 of 6 M HCl to each reservoir to elute the Th from the cartridge. Adjust flow rate to ~1 mL/min. Collect the effluent.

12.3.5 Set centrifuge tubes containing the thorium strip aside for cerium fluoride micro-precipitation.

12.3.6 If Pu measurement is needed, continue with the TEVA separation.

12.3.7 Add 5 mL of 6 M HCl to each reservoir to remove any residual Th isotopes still present (flow rate ~1–2 mL/min). Discard rinse.

12.3.8 Add 5 mL of 3 M HNO_3 to each reservoir to reduce bleed off of organic extraction during Pu strip step (flow rate ~2–4 mL/min).

12.3.9 Place a clean 50 mL polypropylene centrifuge tube labeled with sample number and "Pu" below the appropriate cartridge. Place new yellow tips on TEVA cartridges.

12.3.10 Add 20 mL of the Pu strip solution (0.1 M HCl + 0.05 M HF + 0.01 M $TiCl_3$) to each reservoir (flow rate ~1 mL/min). Collect the effluent.

12.3.11 Set centrifuge tubes containing the plutonium strip aside for cerium fluoride microprecipitation.

12.4 *Purification and Elution of Uranium on TRU resin cartridge*

12.4.1 Fit TRU cartridges with new reservoir.

12.4.2 Rinse the TRU cartridge with 10 mL of 8 M HNO_3 (flow rate ~1–2 mL/min). Discard the effluent.

12.4.3 Add 20 mL of 4 M HCl-0.2 M HF- 0.002 M $TiCl_3$ to each reservoir to remove any Am, Th, or Po (flow rate to ~1-2 mL/minute). Discard the effluent.

12.4.4 Add 5 mL of 3 M HNO_3 to each reservoir (flow rate to ~1–2 mL/min). Discard the effluent. Place new yellow tips on TRU cartridges.

12.4.5 Place a clean 50 mL centrifuge tube labeled with sample number and "U" under each cartridge.

12.4.6 Add 20 mL of 0.1 M of ammonium bioxalate to each cartridge to elute the uranium (flow rate to ~1 mL/minute). Collect the effluent.

12.4.7 Set the centrifuge tubes with the uranium strip aside for cerium fluoride microprecipitation.

12.5 *Purification and Elution of Americium on DGA resin cartridge*

12.5.1 Fit DGA cartridges with new reservoir.

12.5.2 Rinse the DGA cartridge with 5 mL of 6 M HNO_3 (flow rate to 1–2 mL/min). Discard the effluent.

12.5.3 Add 10 mL of 3 M HCl to each reservoir (flow rate ~1–2 mL/min). Discard the effluent.

12.5.4 Add 5 mL of 3 M HNO_3 to each reservoir (flow rate ~1–2 mL/min). Discard the effluent.

12.5.5 Add 20 mL of 0.1 M HNO_3 (flow rate ~1–2 mL/min). Discard the effluent.

12.5.6 Add 10 mL of 0.05 M HNO_3 (flow rate ~2 mL/min). Discard the effluent.

12.5.7 Add 15 mL of 3 M HNO_3/0.25 M HF to each reservoir (flow rate ~1–2 mL/min). Discard the effluent.

12.5.8 Add 3 mL of 3 M HNO_3 to each reservoir (flow rate ~1–2 mL/min). Discard the effluent.

12.5.9 Place a clean 50 mL centrifuge tube labeled with sample number and "Am" under each cartridge.

12.5.10 Add 15 mL of 0.25 M HCl to each reservoir to elute the Am (flow rate ~1 mL/min). Collect the effluent.

12.5.11 Set the centrifuge tubes with the americium strip aside for cerium fluoride microprecipitation.

12.6 *Cerium fluoride microprecipitation*

12.6.1 For collected thorium samples, dilute the Th fraction in the centrifuge tube with deionized water to a volume of 40–45 mL. Add 80 µL of Ce^{+3} carrier. Add 0.5 mL of 30 % H_2O_2. Add 3 mL of 29 M HF. Cap tightly and mix thoroughly. Let the sample sit for at least 15 minutes. Smaller amounts of Ce^{+3} carrier may be used if needed to optimize spectral resolution. It is not recommended to use less than 50 µL of Ce^{+3} carrier. Record the amount of carrier used if different from the prescribed 80 µL.

12.6.2 For collected plutonium samples, add 100 µL of Ce^{+3} carrier. Add 0.5 mL of 30 % H_2O_2. Add 1 mL of 29 M HF. Cap and mix thoroughly. Let the sample sit for at least 15 minutes.

12.6.3 For collected uranium samples, add 100–200 µL of Ce^{+3} carrier. Record the amount of carrier used. Add 0.5 mL of 20 % $TiCl_3$ solution. Add 1 mL of 29 M HF. Cap tightly and mix thoroughly. Let the sample sit for at least 15 minutes.

NOTE: If the natural uranium activity in the sample aliquot is expected to be greater than 15 pCi, it may be advantageous to use 200 µL of Ce^{+3} carrier. Higher levels of natural uranium in samples will consume the Ce^{+3} carrier and will result in lower tracer yields. If lower levels of natural uranium are expected, then 100 µL of Ce^{+3} carrier will be sufficient. The quality of spectral resolution will worsen as the amount of Ce^{+3} carrier increases.

12.6.4 For collected americium samples, add 80 µL of Ce^{+3} carrier. Add 0.5 mL of 30 % H_2O_2. Add 1 mL of 29 M HF. Cap tightly and mix thoroughly. Let the sample sit for at least 15 minutes. Smaller amounts of Ce^{+3} carrier may be used if needed to optimize spectral resolution. It is not recommended to use less than 50 µL of Ce^{+3} carrier. Record the amount of carrier used if different from the prescribed 80 µL.

12.6.5 Prepare filter apparatus.

12.6.6 Rinse the filter chimney with ~5 mL of ethanol to prepare the filter for filtration and test for leaks. If desired, water can be used to check for leaks after the initial ethanol rinse.

12.6.7 Filter the sample containing the desired analysis through the filter apparatus.

12.6.8 Rinse the centrifuge tube that contained the sample with a small amount of water and add rinse to sample.

12.6.9 After the sample has filtered, rinse the filter chimney with ethanol.

12.6.10 Allow the filter to dry.

12.6.11 Prepare the counting source by mounting the filter containing the precipitate on a 32 mm stainless steel planchet fixed with adhesive.

12.6.12 Submit the source to the nuclear counting laboratory for alpha-particle spectrometry.

NOTE: Samples analyzed for thorium must be counted by the second night after the separation step.

13.0 QUALITY CONTROL PROCEDURES

13.1 Reference standards used to provide tracers, spiking solutions, standards, or calibration sources must be obtained from the National Institute of Standards and Technology (NIST) or suppliers who participate in supplying NIST standards or NIST traceable radionuclides.

13.2 For each QC batch of up to 20 samples of the same matrix, the analyst must add the following quality control samples:

13.2.1 method blank

13.2.2 laboratory control sample (LCS)

13.2.2.1 At least one analyte must be included in any LCS. For analytical methods that measure more than one analyte, it is not necessary to include every analyte in the LCS; however, each analyte that is included must be evaluated.

13.2.2.2 The activity of an analyte added to the LCS must be at least ten times the normal expected minimum detectable activity (MDA) for that analyte and should be comparable to sample activities when sample activities in the batch are expected to be higher than ten times the MDA. The spike level should be high enough to ensure that under expected measurement conditions, the relative standard counting uncertainty will not exceed 5 %.

13.2.3 replicate sample (duplicate)

13.3 Analysts are required to control chart results from blanks and laboratory control samples, and to observe the control charts for indicators of possible problems in the measurement system. LIMS software allows the analyst to input data points and to view and print the control charts.

13.4 See the *NAREL Radiochemistry Quality Assurance Manual* (QA/QAM-1) for acceptance criteria for QC samples, and equations for calculating values for quality indicators.

14.0 DATA ANALYSIS AND CALCULATIONS

14.1 All equations shown here represent *values* of quantities, not *numerical values*. To calculate with numerical values, either use coherent units (e.g., SI units) or include the appropriate unit-conversion factors in the equations.

14.2 *Chemical Yield*

14.2.1 To calculate the chemical yield and associated standard uncertainty for an americium, plutonium, uranium, or thorium analysis, use the following equations.

$$Y = \frac{\frac{C_{ST}}{t_S} - \frac{C_{BT}}{t_B}}{\varepsilon \times c_T \times V_T \times D_T \times P_T} \tag{1}$$

$$u(Y) = \sqrt{\frac{\frac{C_{ST}+1}{t_S^2} + \frac{C_{BT}+1}{t_B^2} + \xi_{BT}^2}{\varepsilon^2 c_T^2 V_T^2 D_T^2 P_T^2} + Y^2\left(\frac{u^2(\varepsilon)}{\varepsilon^2} + \frac{u^2(c_T)}{c_T^2} + \frac{u^2(V_T)}{V_T^2} + \frac{u^2(P_T)}{P_T^2}\right)} \tag{2}$$

where

Y	is the chemical yield,
C_{ST}	is the gross (sample) count in the tracer ROI,
C_{BT}	is the background count in the tracer ROI,
t_S	is the length of the sample counting period (usually 1000 min or more),
t_B	is the length of the background counting period (usually 3000 min),
ε	is the alpha-particle detection efficiency,
c_T	is the activity concentration of the tracer solution,
V_T	is the volume of tracer solution added to the sample aliquot,
D_T	is the decay factor for the tracer, which corrects for the decay of the tracer from its reference date and time through the counting period (see below),
P_T	is the alpha-particle emission probability for the tracer ROI, and
ξ_{BT}	is the additional uncertainty of the background correction due to background instability in the tracer ROI (expressed as a count rate)

14.2.2 The decay factor D_T in 14.2.1 is calculated as follows.

$$D_T = e^{-\lambda_T t_{DT}} \times \frac{\sinh(\lambda_T t_S / 2)}{\lambda_T t_S / 2} \tag{3}$$

where

λ_T	is the decay constant for the tracer radionuclide and
t_{DT}	is the elapsed time from the tracer reference date and time to the mid-point of the counting period

NOTE: It is acceptable to use the simpler equation $D_T = e^{-\lambda_T t_{DT}}$ instead of equation 3, because the omitted factor is nearly equal to 1 except in the case of very short-lived radionuclides or very long count times. The same type of simplification may be made to equation 19 below.

14.3 *Activity*

14.3.1 For americium, plutonium, or uranium, use the following equations to calculate the volumic or massic activity of each analyte, and the associated uncertainty.

$$x = \frac{\frac{C_{SA}}{t_S} - \frac{C_{BA}}{t_B}}{\varepsilon \times V_A \times Y \times D_A \times P_A} = \frac{\frac{C_{SA}}{t_S} - \frac{C_{BA}}{t_B}}{\frac{C_{ST}}{t_S} - \frac{C_{BT}}{t_B}} \times \frac{c_T \times V_T \times D_T \times P_T}{V_A \times D_A \times P_A} \tag{4}$$

$$u(x) = \sqrt{\frac{\frac{C_{SA}+1}{t_S^2} + \frac{C_{BA}+1}{t_B^2} + \xi_{BA}^2}{\varepsilon^2 V_A^2 Y^2 D_A^2 P_A^2} + x^2\left(\left(\frac{u^2(Y)}{Y^2} - \frac{u^2(\varepsilon)}{\varepsilon^2}\right) + \frac{u^2(V_A)}{V_A^2} + \frac{u^2(P_A)}{P_A^2} + \varphi_S^2\right)} \tag{5}$$

where

- x is the volumic or massic activity of the analyte,
- C_{SA} is the gross (sample) count in the analyte ROI,
- C_{BA} is the background count in the analyte ROI,
- t_S is the length of the sample counting period,
- t_B is the length of the background counting period,
- ε is the alpha-particle detection efficiency,
- Y is the chemical yield (equation 1),
- V_A is the size of the sample aliquot (e.g., volume or mass),
- D_A is the decay factor for the analyte, which corrects for decay of the analyte from the reference date and time through the counting period (see below),
- P_A is the alpha-particle emission probability for the analyte ROI,
- $\breve{\varsigma}_{BA}$ is the additional uncertainty of the background correction due to background instability in the analyte ROI (expressed as a count rate), and
- φ_S is the relative standard uncertainty due to subsampling

If the aliquot size V_A is a mass, then

$$\varphi_S = \sqrt{\frac{(0.4\text{g/cm}^3)d^3}{m_S}}$$

where

- d = 0.1 cm, and
- m_S is the mass of sample dissolved

If the aliquot size is a volume or if it is 1 SAMP or 1 FILT, then $\varphi_S = 0$.
In all other cases φ_S is assumed by default to be 0.05.

14.3.2 For thorium isotopes, use the following equation to calculate the volumic or massic activity of each analyte.

$$x = \frac{\frac{C_{SA}}{t_S} - \frac{C_{BA}}{t_B} - R_I}{\varepsilon \times V_A \times Y \times D_A \times P_A} = \frac{\frac{C_{SA}}{t_S} - \frac{C_{BA}}{t_B} - R_I}{\frac{C_{ST}}{t_S} - \frac{C_{BT}}{t_B}} \times \frac{c_T \times V_T \times D_T \times P_T}{V_A \times D_A \times P_A} \quad (6)$$

where R_I denotes the count rate due to interference from the ^{229}Th tracer. The value of R_I is calculated as shown below.

$$R_I = R_{NT} \times \left(SF + \frac{c_I \times D_I \times P_A}{c_T \times D_T \times P_T} \right) \quad (7)$$

where

- R_{NT} is the tracer net count rate, $C_{ST}/t_S - C_{BT}/t_B$
- SF is the tracer-into-analyte spillover factor (ratio of count rates)
- c_I is the activity concentration of analyte (contaminant) in the tracer
- D_I is the decay factor for the contaminant (from the tracer reference date through the counting period)

The value of SF is assumed to be zero for all isotopes except ^{230}Th.

14.3.3 To obtain the combined standard uncertainty of x, perform the following calculations:

$$A = \frac{R_{NA}}{R_{NT}} - SF, \quad B = \frac{c_T \times D_T \times P_T}{P_A}, \quad \text{and} \quad C = c_I \times D_I \tag{8}$$

$$u^2(A) = \frac{u^2(R_{NA})}{R_{NT}^2} + \frac{R_{NA}^2}{R_{NT}^4} u^2(R_{NT}) + u^2(SF) \tag{9}$$

$$u^2(B) = B^2 \times \left(u_r^2(c_T) + u_r^2(P_T) + u_r^2(P_A)\right) \tag{10}$$

$$u^2(C) = D_I^2 \times u^2(c_I) \tag{11}$$

$$u(x) = \sqrt{\left(u^2(A) \times B^2 + A^2 \times u^2(B) + u^2(C)\right) \times \frac{V_T^2}{V_A^2 \times D_A^2} + x^2 \times \left(u_r^2(V_T) + u_r^2(V_A) + \varphi_S^2\right)} \tag{12}$$

where R_{NA} denotes the net count rate in the analyte ROI, $C_{SA} / t_S - C_{BA} / t_B$.

14.3.4 The decay factor D_A in 14.3.1 is calculated as follows.

$$D_A = e^{-\lambda_A t_{DA}} \times \frac{\sinh(\lambda_A t_S / 2)}{\lambda_A t_S / 2} \tag{13}$$

where

λ_A is the decay constant for the analyte and
t_{DA} is the elapsed time from the reference date and time to the midpoint of the counting period ($t_{DA} = t_S / 2$ if the reference date and time equals the start of counting)

Equation 19 may also be simplified in the manner described in the note below Equation 3.

14.4 For all analyses and isotopes, use the following equations to calculate the critical net count rate and the critical value of the massic or volumic activity.

$$S_C = 0.4 \times \left(\frac{1}{t_B} - \frac{1}{t_S}\right) + \frac{z_{0.95}^2}{4} \times \left(\frac{1}{t_S} + \frac{1}{t_B}\right) + z_{0.95} \sqrt{\frac{C_{BA} + 0.4}{t_B} \times \left(\frac{1}{t_S} + \frac{1}{t_b}\right) + \frac{R_I}{t_S} + u^2(R_I) + \xi_{BA}^2} \tag{14}$$

$$x_C = \frac{S_C}{\varepsilon \times V_A \times Y \times D_A \times P_A} \tag{15}$$

where

S_C is the critical net count rate,
x_C is the critical massic or volumic activity,
$z_{0.95}$ is 1.645, the 95th percentile of the standard normal distribution, and

where all other symbols are as defined above. These critical values are calculated for each analysis and analyte. A detection decision for each analyte may be made by comparing the analyte's net count rate to S_C or by comparing its activity x to x_C.

14.5 Use the following equation to calculate the minimum detectable activity (volumic or massic activity) for each analyte.

$$x_D = \frac{\frac{z_{0.95}^2}{2t_S} + S_C + z_{0.95}\sqrt{\frac{z_{0.95}^2}{4t_S^2} + S_C\left(\frac{1}{t_S} + \frac{z_{0.95}^2\varphi_S^2}{t_B}\right) + R_{BA}\left(\frac{1}{t_S} + \frac{1}{t_B}\right) + \frac{R_I}{t_S} + u^2(R_I) + \xi_{BA}^2}}{\varepsilon \times V_A \times Y \times D_A \times P_A \times (1 - z_{0.95}^2\varphi_S^2)} \quad (16)$$

where

x_D is the minimum detectable activity,
R_{BA} is the background count rate in the analyte ROI,
S_C is an estimate of the critical net count rate calculated using equation 20 with $C_{BA} = R_{BA}t_B$, and
$z_{0.95}$ is 1.645, the 95th percentile of the standard normal distribution

For all analysis types except thorium, set both R_I and its uncertainty $u(R_I)$ equal to 0. For thorium analyses calculate $u^2(R_I)$ as follows

$$u^2(R_I) = u^2(R_{NT})\left(SF + \frac{c_I \times D_I \times P_A}{c_T \times D_T \times P_T}\right)^2 + R_{NT}^2\left(u^2(SF) + \left(\frac{c_I \times D_I \times P_A}{c_T \times D_T \times P_T}\right)^2\left(\frac{u^2(c_I)}{c_I^2} + \frac{u^2(c_T)}{c_T^2}\right)\right) \quad (17)$$

Note that $SF = u(SF) = 0$ all thorium isotopes except ^{230}Th.

15.0 DATA REVIEW

15.1 *General Procedure*

15.1.1 See *NAREL Standard Operating Procedure for Review of Radiochemistry Data* (DR/SOP-2) for general procedures for data review.

15.1.2 The alpha-spectrometry instrument operator or another person designated by the Nuclear Counting Laboratory (NCL) Team Leader performs a preliminary review of all alpha-spectrometry data.

15.1.3 After the preliminary review, the NCL returns all documentation to the analyst, who performs the first complete review of the data. The analyst runs the Alpha Review software to perform data reduction and to review the results and store them in the LIMS database.

NOTE: If the analyst is unavailable to perform the first review, another qualified employee may perform it using the Alpha Review software.

15.2 *Preliminary Data Review in the NCL*

15.2.1 The NCL reviewer checks the data entry for each analysis by comparing the values printed on the report to the values provided by the analyst on the assay batch form. He or she also checks that the sample count time is correct.

15.2.2 The NCL reviewer checks that the calibration was current, the background was current and within acceptable limits, and that other instrument QC results were current and acceptable.

15.2.3 The NCL reviewer checks that the source was placed at an appropriate shelf height in the alpha-spectrometry chamber.

15.2.4 The NCL reviewer checks that the background level for each ROI meets the established acceptance criteria as described in NC/SOP-8.

15.2.5 The NCL reviewer checks the spectrum from each actinide analysis and judges the reasonableness of the results. These checks are based on the report and spectrum graph printed by commercial analysis software.

15.2.6 When there is evidence of a gain shift that moves the centroids of analyte and tracer peaks, the NCL reviewer may either adjust the ROIs manually or recount the source on a different detector. If the ROIs are manually adjusted, the reviewer notes it on the printout. In all cases the NCL takes corrective action to eliminate the gain shift or, if necessary, to remove the detector from operation.

15.2.7 When the preliminary data review is complete, the NCL reviewer initials and dates the printouts from the commercial analysis software. The reviewer returns the assay batch form, the printouts from the commercial analysis software, and any other data sheets to the analyst.

15.3 *Actinide Data Review*

15.3.1 While using Alpha Review, the analyst (or other first reviewer) double-checks the sample and tracer information, including the sample number, aliquot size and units, tracer identification number, tracer reference date, tracer concentration, amount of tracer used, and, if applicable, the separation date and time.

15.3.2 The Alpha Review program automatically selects the detector's most recent calibration from the LIMS, although the analyst can manually choose the current calibration for a different shelf number if necessary. The program displays the shelf number, efficiency, uncertainty, and calibration date for inspection.

15.3.3 The analyst checks that each peak present in the spectrum is at the expected location within its ROI and that peaks do not spill over significantly from one ROI into another.

15.3.4 If the spectrum is smeared (i.e., if the peaks have poor resolution or large tails), the analyst should either reanalyze the sample or request a recount of the source. In some cases, a recount may be a first step to determine whether a reanalysis is necessary, but a recount should not be requested if the problem is clearly due to source preparation and not the instrument.

15.3.5 If unknown peaks are in the spectrum, the analyst identifies them by their energies. If the peaks are caused by breakthrough due to high concentrations, the analyst should reanalyze the sample using a smaller aliquot or more appropriate reagents.

15.3.6 Using Alpha Review, the analyst checks that the instrument calibration was current.

15.3.7 Using Alpha Review, the analyst checks that the FWHM for any peak with adequate counting statistics does not exceed 100 keV. Alpha Review performs this check automatically whenever the net count for the peak is greater than three times its associated standard uncertainty.

15.3.8 Using Alpha Review, the analyst checks that the chemical yield of the analysis meets the criteria described in the *NAREL Radiochemistry Quality Assurance Manual* (QA/QAM-1). If the yield does not meet the stated criteria, the reviewer must disapprove the analysis for reporting. See the *NAREL Standard Operating Procedure for Review of Radiochemistry Data* (DR/SOP-2) for further instructions in this case.

15.3.9 Using Alpha Review, the analyst checks that the net activity for each analyte is not less than zero by an amount that is statistically significant at the 1 % level. If a result is less than zero by a statistically significant amount, the reviewer must qualify the result as "rejected." See the *NAREL Standard Operating Procedure for Review of Radiochemistry Data* (DR/SOP-2) for further instructions in this case.

15.3.10 Alpha Review automatically performs the objective tests described above and generates warnings for each failed test. The program also generates a printout for each completed analysis, showing raw data and results, any automatically generated warning messages, comments by the data reviewer, and the disposition selected by the reviewer (either approval or disapproval).The Alpha Review printout indicates whether the reviewer approved or disapproved the results for reporting. When results are disapproved, the program requires the reviewer to provide the reason or reasons in the form of a comment, which is shown on the Alpha Review printout.

15.3.11 The analyst notes any abnormalities. If abnormalities are observed, the analyst should discuss them with the NCL personnel. When the review is complete, the analyst initials and dates the printouts from the analysis software and Alpha Review.

15.3.12 The RDC, the second official reviewer in the LIMS database, performs an independent final review of the results after they have been stored in the LIMS and the analyst has submitted all documentation. The RDC also initials and dates the software printouts and indicates agreement or disagreement with the judgment of the first reviewer. Differences of opinion must be resolved before the results may be reported.

15.4 *Thorium*

15.4.1 Since the alpha-particle energies for ^{229}Th/^{230}Th are not widely separated, the reviewer examines each thorium spectrum carefully for spillover from one ROI into another.

15.4.2 Thorium sources should never be analyzed on the topmost shelf in the spectrometer, because proximity to the detector tends to degrade peak resolution. The reviewer checks that the selected shelf height is appropriate for a thorium source.

15.4.3 In most solid samples, ^{232}Th and ^{228}Th occur in approximate equilibrium.

15.5 *Americium*

15.5.1 Since the alpha-particle energies for ^{243}Am/^{241}Am are not widely separated, the reviewer examines each americium spectrum carefully for spillover from one ROI into another.

15.5.2 Americium sources should never be analyzed on the topmost shelf in the spectrometer, because proximity to the detector tends to degrade peak resolution. The reviewer checks that the selected shelf height is appropriate for an americium source.

15.6 *Plutonium*

15.6.1 Plutonium-238 is seldom found in environmental media at levels that are detectable by this method. NAREL commonly performs a confirmatory analysis for plutonium whenever the measured result for ^{238}Pu exceeds its estimated 3-sigma uncertainty.

15.6.2 If the ^{238}Pu activity in an unspiked sample is greater than its estimated 3-sigma expanded uncertainty, the reviewer must report the measured value to the Nuclear Counting Laboratory Team Leader and the RDC, and, if the sample is from the RadNet network, the reviewer must submit a RadNet Event Report.

15.7 *Uranium*

15.7.1 In most solid samples, ^{234}U and ^{238}U should exist in approximate radioactive equilibrium. In naturally occurring uranium, the ^{235}U activity should be about 5 % of the activity of ^{234}U or ^{238}U.

15.7.2 If unusual ratios of uranium isotopes are measured, the reviewer should investigate and report the results to the Nuclear Counting Laboratory Team Leader.

16.0 RECORDS MANAGEMENT

16.1 The following documents are generated during this procedure:

- Actinide logbook pages
- Reagent logbook pages
- Raw data sheets generated from the NCL
- Alpha review sheets
- Assay batch forms
- QC batch reports
- Reagent blank control charts
- LCS control charts
- Analytical check lists

16.2 Original copies of all records and documents are delivered to the Radiochemistry Data Coordinator after review, for files or inclusion in client data packages. Copies of applicable logbook pages are also delivered to the Radiochemistry Data Coordinator as part of the data package.

17.0 METHOD PERFORMANCE

17.1 Method performance was evaluated in accordance with *NAREL Standard Operating Procedure for Initial Evaluation of an Analytical Method* (QA/SOP-3).

17.2 Each year, analysts analyze performance testing samples as a measure of continual monitoring of method performance. Results and data are on file with the NAREL QA Manager.

17.3 *Measurement Quality Objectives* (*MQOs*)

17.3.1 Calculate the required minimum detectable concentration (MDC) and minimum quantifiable concentration (MQC) for routine analyses using the following parameters and appropriate equations from section 14.0. Assume a 1 g aliquot, 50 % yield, 15 % efficiency, 1000 min sample count time, 3000 min background

count time, and the maximum tolerable background count rate for each analyte's ROI. With these parameters, the MDCs and MQCs are as shown below.

Analyte	MDC / (pCi/g)	MQC / (pCi/g)
^{238}Pu, ^{239}Pu	0.08	1.2
^{230}Th	0.14	1.2
^{235}U	0.12	N/A*
^{232}Th, ^{234}U, ^{238}U	0.10	1.2

* For ^{235}U, the relative standard uncertainty always exceeds 10 %.

17.3.2 CERLS may adjust the aliquot size and count time as necessary to meet other specified MQOs.

17.4 *Method Validation Sample Data*

17.4.1 Plutonium

MAPEP 26 Soil	Result	CSU	Target	%R	Z
Pu-238	3.303	0.190	3.676	89.9%	-1.96
	3.378	0.189	3.676	91.9%	-1.58
	3.627	0.203	3.676	98.7%	-0.24
	3.648	0.206	3.676	99.2%	-0.13
	3.461	0.193	3.676	94.2%	-1.11
	3.644	0.204	3.676	99.1%	-0.16
	3.376	0.189	3.676	91.8%	-1.59
Pu-239	1.692	0.112	1.778	95.1%	-0.77
	1.670	0.108	1.778	93.9%	-1.00
	1.692	0.111	1.778	95.1%	-0.78
	1.880	0.121	1.778	105.7%	0.84
	1.698	0.109	1.778	95.5%	-0.74
	1.801	0.116	1.778	101.3%	0.20
	1.716	0.111	1.778	96.5%	-0.56

MAPEP 27 Soil	Result	CSU	Target	%R	Z
Pu-238	3.370	0.214	2.936	114.8%	2.03
	2.833	0.168	2.936	96.5%	-0.61
	2.806	0.165	2.936	95.6%	-0.79
	2.578	0.152	2.936	87.8%	-2.35
	3.001	0.185	2.936	102.2%	0.35
	2.904	0.172	2.936	98.9%	-0.18
	2.713	0.162	2.936	92.4%	-1.37
Pu-239	4.259	0.261	3.718	114.5%	2.07
	3.760	0.214	3.718	101.1%	0.20
	3.344	0.191	3.718	89.9%	-1.96

MAPEP 27 Soil	Result	CSU	Target	%R	Z
	3.467	0.195	3.718	93.2%	-1.29
	3.782	0.225	3.718	101.7%	0.28
	3.676	0.210	3.718	98.9%	-0.20
	3.720	0.211	3.718	100.1%	0.01

MAPEP 30 Soil	Result	CSU	Target	%R	Z
Pu-238	2.72	0.143	2.773	98.1%	-0.37
	2.65	0.142	2.773	95.6%	-0.87
	2.65	0.139	2.773	95.6%	-0.89
	2.44	0.129	2.773	88.0%	-2.58
	2.41	0.131	2.773	86.9%	-2.77
	2.88	0.148	2.773	103.8%	0.72
	2.53	0.141	2.773	91.2%	-1.73
Pu-239	1.990	0.111	2.219	89.7%	-2.06
	2.200	0.122	2.219	99.2%	-0.15
	2.070	0.113	2.219	93.3%	-1.32
	1.900	0.105	2.219	85.6%	-3.03
	1.970	0.112	2.219	88.8%	-2.22
	2.200	0.119	2.219	99.2%	-0.16
	1.990	0.117	2.219	89.7%	-1.95

MAPEP 32 Soil	Result	CSU	Target	%R	Z
Pu-238	2.612	0.172	2.316	112.8%	1.72
	2.415	0.148	2.316	104.3%	0.67
	2.410	0.154	2.316	104.1%	0.61
	2.299	0.143	2.316	99.3%	-0.12
	2.155	0.134	2.316	93.0%	-1.20
	2.259	0.150	2.316	97.5%	-0.38
	2.241	0.137	2.316	96.8%	-0.55
Pu-239	2.104	0.145	1.954	107.7%	1.03
	1.970	0.125	1.954	100.8%	0.12
	1.947	0.130	1.954	99.6%	-0.06
	1.729	0.114	1.954	88.5%	-1.98
	1.783	0.115	1.954	91.2%	-1.49
	1.855	0.128	1.954	94.9%	-0.78
	1.792	0.115	1.954	91.7%	-1.41

MAPEP 33 Soil	Result	CSU	Target	%R	Z
Pu-238	2.564	0.155	2.699	95.0%	-0.87
	2.641	0.166	2.699	97.8%	-0.35
	3.032	0.198	2.699	112.3%	1.68
	2.659	0.162	2.699	98.5%	-0.25
	2.673	0.162	2.699	99.0%	-0.16
	2.867	0.176	2.699	106.2%	0.95
	2.820	0.177	2.699	104.5%	0.68
Pu-239	2.002	0.127	2.226	89.9%	-1.76
	2.190	0.142	2.226	98.4%	-0.25
	2.413	0.164	2.226	108.4%	1.14
	2.060	0.131	2.226	92.5%	-1.27
	2.287	0.143	2.226	102.7%	0.43
	2.214	0.142	2.226	99.5%	-0.08
	2.335	0.151	2.226	104.9%	0.72

Rocky Flats Run 2 Soil	Result	CSU	Target	%R	Z
Pu-239	9.702	0.448	10.187	95.2%	-1.08
	8.979	0.445	10.605	84.7%	-3.65
	9.613	0.449	9.707	99.0%	-0.21
	9.841	0.474	9.751	100.9%	0.19
	8.865	0.413	9.567	92.7%	-1.70
	9.104	0.448	9.963	91.4%	-1.92
	8.937	0.410	9.888	90.4%	-2.32

Method Blanks	Result	CSU	Target	%R	Z
Pu-238	0.007905	0.00706	0	n/a	1.12
	0.002054	0.00681	0	n/a	0.30
	-0.010070	0.00735	0	n/a	-1.37
	-0.001171	0.00388	0	n/a	-0.30
	0.003250	0.00603	0	n/a	0.54
	0.009962	0.00776	0	n/a	1.28
	-0.010290	0.00547	0	n/a	-1.88
Pu-239	0.009034	0.00799	0	n/a	1.13
	0.000000	0.00482	0	n/a	0.00
	0.004475	0.00613	0	n/a	0.73
	0.003514	0.00511	0	n/a	0.69
	-0.001083	0.00359	0	n/a	-0.30

Method Blanks	Result	CSU	Target	%R	Z
	0.006641	0.00586	0	n/a	1.13
	0.003858	0.00716	0	n/a	0.54

17.4.2 Thorium

MAPEP 30 SOIL	Result	CSU	Target	%R	Z
Th-228	1.38	0.096	1.475	93.6%	-0.99
	1.39	0.093	1.475	94.2%	-0.91
	1.43	0.099	1.475	96.9%	-0.46
	1.41	0.0966	1.475	95.6%	-0.67
	1.48	0.102	1.475	100.3%	0.05
	1.44	0.096	1.475	97.6%	-0.37
	1.59	0.107	1.475	107.8%	1.07
Th-230	3.01	0.18	2.779	108.3%	1.28
	2.85	0.167	2.779	102.6%	0.42
	2.86	0.174	2.779	102.9%	0.47
	2.71	0.164	2.779	97.5%	-0.42
	2.82	0.171	2.779	101.5%	0.24
	2.83	0.166	2.779	101.8%	0.31
	2.68	0.163	2.779	96.4%	-0.61
Th-232	1.40	0.097	1.411	99.2%	-0.11
	1.49	0.098	1.411	105.6%	0.81
	1.38	0.097	1.411	97.8%	-0.32
	1.47	0.100	1.411	104.2%	0.59
	1.39	0.097	1.411	98.5%	-0.22
	1.37	0.092	1.411	97.1%	-0.44
	1.42	0.098	1.411	100.6%	0.09

Rocky Flats Run 2 SOIL	Result	CSU	Target	%R	Z
Th-228	2.037	0.0328	1.9455	104.7%	2.79
	1.898	0.118	1.9455	97.6%	-0.40
	1.951	0.126	1.9455	100.3%	0.04
	1.933	0.125	1.9455	99.4%	-0.10
	1.807	0.11	1.9455	92.9%	-1.26
	2.013	0.129	1.9455	103.5%	0.52
	2.055	0.131	1.9455	105.6%	0.84
Th-230	9.518	0.497	9.344	101.9%	0.35
	9.519	0.486	9.907	96.1%	-0.80
	10.39	0.546	10.045	103.4%	0.63

Rocky Flats Run 2 SOIL	Result	CSU	Target	%R	Z
	10.28	0.545	9.624	106.8%	1.20
	8.417	0.421	9.513	88.5%	-2.60
	10.72	0.564	10.094	106.2%	1.11
	10.6	0.557	9.957	106.5%	1.15
Th-232	1.772	0.114	1.9455	91.1%	-1.52
	1.912	0.119	1.9455	98.3%	-0.28
	1.958	0.126	1.9455	100.6%	0.10
	2.208	0.139	1.9455	113.5%	1.89
	1.896	0.114	1.9455	97.5%	-0.43
	2.188	0.138	1.9455	112.5%	1.76
	2.031	0.129	1.9455	104.4%	0.66

Method Blanks	Result	CSU	Target	%R	Z
Th-228	-0.00293	0.00594	0	n/a	-0.49
	0.01236	0.00700	0	n/a	1.77
	0.00858	0.00845	0	n/a	1.02
	0.00645	0.00776	0	n/a	0.83
	0.00873	0.00772	0	n/a	1.13
	0.00096	0.00647	0	n/a	0.15
	0.00410	0.00664	0	n/a	0.62
Th-230	0.01967	0.0167	0	n/a	1.18
	0.03400	0.0182	0	n/a	1.87
	0.03174	0.0183	0	n/a	1.73
	0.03400	0.0187	0	n/a	1.82
	0.00853	0.0163	0	n/a	0.52
	0.02313	0.0171	0	n/a	1.35
	0.02039	0.0170	0	n/a	1.20
Th-232	0.009754	0.00677	0	n/a	1.44
	0.009265	0.00722	0	n/a	1.28
	0.01929	0.00938	0	n/a	2.06
	0.01074	0.00746	0	n/a	1.44
	0	0.00345	0	n/a	0.00
	0.01157	0.00736	0	n/a	1.57
	0.01228	0.00696	0	n/a	1.76

17.4.3 Uranium

MAPEP 30 SOIL	Result	CSU	Target	%R	Z
U-234	2.488	0.161	2.340	106.3%	0.92
	2.458	0.147	2.340	105.0%	0.80
	2.373	0.147	2.340	101.4%	0.22
	2.397	0.147	2.340	102.4%	0.39
	2.362	0.142	2.340	100.9%	0.16
	2.256	0.134	2.340	96.4%	-0.63
	2.106	0.134	2.340	90.0%	-1.75
U-238	2.417	0.157	2.398	100.8%	0.12
	2.186	0.134	2.398	91.2%	-1.58
	2.490	0.153	2.398	103.8%	0.60
	2.412	0.147	2.398	100.6%	0.10
	2.534	0.151	2.398	105.7%	0.90
	2.366	0.139	2.398	98.7%	-0.23
	2.379	0.147	2.398	99.2%	-0.13

Rocky Flats Run 2 SOIL	Result	CSU	Target	%R	Z
U-234	9.646	0.51000	9.86	97.8%	-0.42
	9.752	0.49300	9.80	99.6%	-0.09
	9.433	0.46200	9.81	96.1%	-0.82
	9.891	0.49100	10.00	98.9%	-0.22
	9.789	0.47200	10.33	94.7%	-1.15
	10.400	0.51600	10.08	103.1%	0.61
	10.190	0.50600	10.02	101.7%	0.34
U-238	10.050	0.530	10.03	100.2%	0.04
	9.768	0.493	9.97	98.0%	-0.41
	9.302	0.456	9.98	93.2%	-1.49
	10.100	0.501	10.18	99.2%	-0.16
	9.773	0.472	10.51	93.0%	-1.56
	10.220	0.507	10.26	99.6%	-0.08
	10.460	0.519	10.92	95.8%	-0.89
U-235	0.432900	0.0550	0.46	94.1%	-0.49
	0.517600	0.0591	0.46	112.5%	0.97
	0.470800	0.0531	0.46	102.3%	0.20
	0.544400	0.0602	0.47	115.8%	1.24
	0.500800	0.0545	0.49	102.2%	0.20
	0.537900	0.0598	0.48	112.1%	0.97
	0.521900	0.0584	0.47	111.0%	0.89

Method Blanks	Result	CSU	Target	%R	Z
U-234	0.055880	0.01590	0	n/a	3.51
	0.026410	0.01170	0	n/a	2.26
	0.004921	0.00674	0	n/a	0.73
	0.040830	0.01300	0	n/a	3.14
	0.012700	0.00794	0	n/a	1.60
	0.009867	0.00873	0	n/a	1.13
	0.026190	0.01070	0	n/a	2.45
U-238	0.02079	0.0106	0	n/a	1.96
	0.01760	0.0104	0	n/a	1.69
	0.02215	0.0099	0	n/a	2.24
	0.01237	0.0086	0	n/a	1.44
	0.01617	0.0087	0	n/a	1.87
	0.02467	0.0107	0	n/a	2.31
	0.02369	0.0108	0	n/a	2.19
U-235	0.026460	0.01270	0	n/a	2.08
	0.010540	0.00944	0	n/a	1.12
	0.007367	0.00795	0	n/a	0.93
	0.002964	0.00663	0	n/a	0.45
	0.004149	0.00604	0	n/a	0.69
	0.000000	0.00467	0	n/a	0.00
	0.019420	0.01140	0	n/a	1.70

18.0 POLLUTION PREVENTION

18.1 Pollution prevention encompasses any technique that reduces or eliminates the quantity and/or toxicity of waste at the point of generation. Numerous opportunities for pollution prevention exist in laboratory operations. The EPA places pollution prevention as the management option of first choice.

18.2 Volumes of prepared reagents are made in the smallest amounts consistent with sample batch sizes to minimize having to discard unused reagents.

19.0 WASTE MANAGEMENT

19.1 The EPA requires that laboratory waste management practices be conducted consistent with all applicable rules and regulations. It is the responsibility of each laboratory to assure adherence to EPA regulations. Specific information can be found in the *NAREL Chemical Hygiene Plan* (HS/M-2).

19.2 The waste stream generated from analyzing one sample for the previously described procedure is 25 mL of 12 M hydrochloric acid, 8 mL of 16 M nitric acid, 2 mL of 29 M hydrofluoric acid, 0.04 g of sodium nitrite, 0.19 g of oxalic acid, 2 g of aluminum nitrate, and 0.29 g of ammonium oxalate.

19.3 Acidic waste solutions are collected in a bucket, neutralized, and poured down the drain.

20.0 REFERENCES

20.1 *Rapid Radiochemical Method for Isotopic Uranium in Building Materials for Environmental Remediation Following Radiological Incidents.* http://www.epa.gov/narel/rapid_methods.html.

20.2 *Rapid Radiochemical Method for Plutonium-238 and Plutonium-239/240 in Building Materials for Environmental Remediation Following Radiological Incidents.* http://www.epa.gov/narel/rapid_methods.html.

20.3 *Rapid Radiochemical Method for Americium-241 in Building Materials for Environmental Remediation Following Radiological Incidents.* http://www.epa.gov/narel/rapid_methods.html.

20.4 *NAREL Standard Operating Procedure for Preparation of Self-Cleaning U-232 Tracer Solution* (AMS/SOP-6).

20.5 *NAREL Standard Operating Procedure for Preparing and Validating Radiochemical Tracers, Spiking Solutions, and Calibration Solutions* (QA/SOP-4).

20.6 *NAREL Chemical Hygiene Plan* (HS/M-2).

20.7 *NAREL Radiation Safety Manual* (HS/M-1).

20.8 *NAREL Standard Operating Procedure for Calibration, Use, and Maintenance of Pipets* (SE/SOP-4).

20.9 *NAREL Standard Operating Procedure for Maintenance and Use of Balances* (SE/SOP-1).

20.10 *NAREL Standard Operating Procedure for Calibration and Use of Alpha Spectrometers Using AlphaVision* (NC/SOP-8).

20.11 *NAREL Standard Operating Procedure for Microwave Digestion of Samples for Actinide, Strontium, Radium, and Alpha/Beta Analyses* (AMS/SOP-7).

20.12 *NAREL Standard Operating Procedure for Initial Evaluation of an Analytical Method* (QA/SOP-3).

20.13 *NAREL Radiochemistry Quality Assurance Manual* (QA/QAM-1).

20.14 *NAREL Standard Operating Procedure for Review of Radiochemistry Data* (DR/SOP-2).

20.15 *NAREL Common Terminology* (DR/T-1).

21.0 APPENDICES (TABLES, DIAGRAMS, AND FLOWCHARTS)

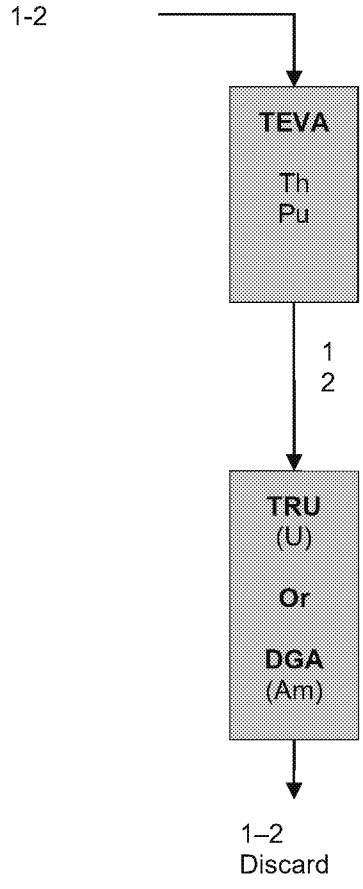
21.1 Actinides Separation Scheme – Part 1.

21.2 Actinides Separation Scheme for Pu, Th and U – Parts 2 and 3.

21.3 Actinides Separation Scheme for Pu, Th and Am – Parts 4 and 5.

Appendix 21.1

ACTINIDES SEPARATION SCHEME – Part 1



With cartridges in tandem:

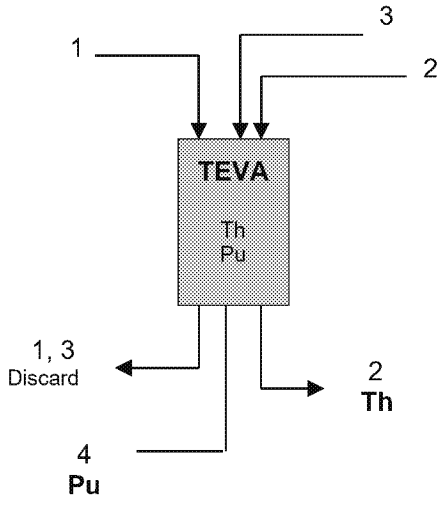
1. Load solution:
   Digested sample, Fe^{+3},
   ascorbic acid, $NaNO_2$.
   Elements are loaded in the following valence states:
   - Pu^{+4}
   - Th^{+4}
   - U^{+6}
   - Am^{+3}

   Discard eluent.

2. Rinse with 3 M HNO_3

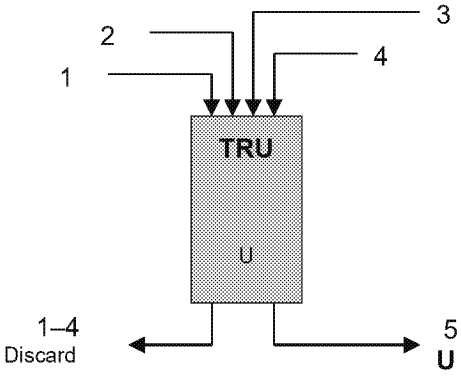
Appendix 21.2

ACTINIDES SEPARATION SCHEME FOR Pu, Th AND U – Parts 2 and 3



TEVA cartridge only:

1. Rinse with 3 M HNO_3. Discard.
2. Elute Th with 6 M HCl.
3. Rinse with 3 M HNO_3. Discard.
4. Elute Pu with 0.1 M HCl / 0.05 M HF / 0.01 M $TiCl_3$.

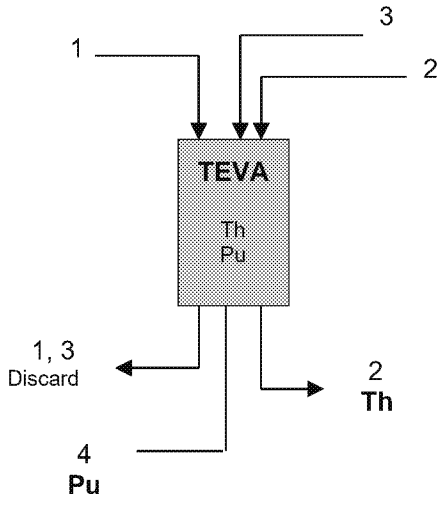


TRU cartridge only:

1. Rinse with 3 M HNO_3. Discard.
2. Rinse with 8 M HNO_3. Discard.
3. Rinse with 4 M HCl-0.2 M HF-.002 M $TiCl_3$. Discard.
4. Rinse with 3 M HNO_3. Discard.
5. Elute U with 0.1 M ammonium bioxalate.

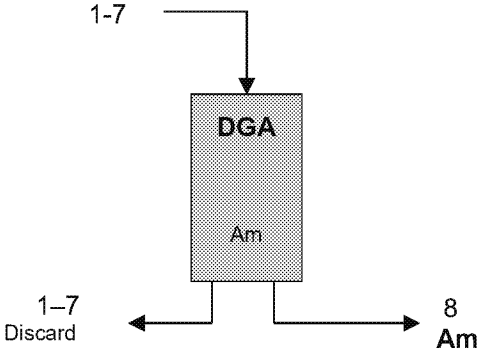
Appendix 21.3

ACTINIDES SEPARATION SCHEME FOR Pu, Th AND Am – Parts 4 and 5



TEVA cartridge only:

1. Rinse with 3 M HNO_3. Discard.
2. Elute Th with 6 M HCl.
3. Rinse with 3 M HNO_3. Discard.
4. Elute Pu with 0.1 M HCl / 0.05 M HF / 0.01 M $TiCl_3$.



DGA cartridge only:

1. Rinse with 6 M HNO_3. Discard.
2. Rinse with 3 M HCl. Discard.
3. Rinse with 3 M HNO_3. Discard.
4. Rinse with 0.1 M HNO_3. Discard.
5. Rinse with 0.05 M HNO_3. Discard.
6. Rinse with 3 M HNO_3 / 0.25 M HF. Discard.
7. Rinse with 3 M HNO_3. Discard.
8. Elute Am with 0.25 M HCl.